Studies on Acrylonitrile Butadiene Rubber/Reclaimed Rubber Blends

T. D. SREEJA AND S. K. N. KUTTY*

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Cochin 682 022, India

ABSTRACT: Cure characteristics and mechanical properties of acrylonitrile butadiene rubber/reclaimed rubber blends were studied. Minimum torque, (maximum –minimum) torque, scorch time, cure time and cure rate decreased in presence of reclaimed rubber. Tensile strength, elongation at break and compression set increased with increase in reclaim content. Resilience and abrasion resistance decreased with reclaim loading. Heat build up was higher for the blends. The ageing resistance of the blends was inferior to that of the gum compound.

KEY WORDS: acrylonitrile butadiene rubber, reclaimed rubber, blend, mechanical properties.

INTRODUCTION

THE DISPOSAL OF waste tyre has become a great environmental concern globally due to the growing stock piles of used tyres and corresponding increase of disposal charge for discarded tyres. In the last few years considerable work has been done on reuse of scrap rubber by chemical [1,2], thermomechanical [3,4], and cryomechanical process [5–7]. Accepta and Vergnaud [8,9] have developed a process to improve the quality of scrap rubber powder recovered from old tyres. A number of reviews on recycling and reuse of elastomers have been reported

---

*Author to whom correspondence should be addressed. E-mail: sunil@cusat.ac.in

0095-2443/02/02 0145–11 $10.00/0 DOI: 10.1106/009524402024278

[10–16]. Processing characteristics and mechanical properties of rubber vulcanizates containing ≤55% reclaimed rubber have been reported by Magryta [17]. Gibala and Hamed have studied the cure characteristics and the mechanical behaviour of rubber compounds containing ground vulcanizates [18]. The effect of ground rubber on EPDM vulcanizates has studied by Seo and Lim [19].

Theodore et al. have reported the cure and mechanical properties of elastomeric compound containing devulcanized material [20]. It has been reported that upto 20% reclaimed rubber could be used in place of natural rubber in blends without greatly affecting the mechanical properties of products [21]. Phadke et al. reported that addition of cryoground rubber in natural rubber caused a change in cure characteristics and showed a detrimental effect on most vulcanizate properties [22]. Chopey [23] and Burgogne et al. [24] have shown that there was a significant drop in tensile strength when powdered rubber was added to conventional rubber compound. Phadke et al. [4] have reported that poor physical properties and processing characteristics of reclaimed rubber vulcanizates could be improved by blending with fresh rubber. However, a systematic study on the utilization of reclaimed rubber to prepare a blend using NBR has found in the open literature. This work is an attempt in this direction.

EXPERIMENTAL

Materials used

NBR was obtained from Apar Polymers Ltd., India. Reclaim (WTR) was supplied by Kerala Rubber and Reclaims, Mamala, India. The characteristics of reclaim used are given in Table 1. Zinc oxide (ZnO) was obtained from M/s, Meta Zinc Ltd, Bombay. Stearic acid was procured from Godrej Soap (Pvt) Ltd., Bombay, Dibenzothiazyl disulfide (MBTS) & 1,2-dihydro 2,2,4-trimethyl quinoline (HS) were obtained from Bayer India Ltd., Bombay. Tetramethylthiuramdisulfide (TMTD) was supplied by NOCIL, Bombay, India. Sulfur was supplied by Standard Chemical Company Private Ltd., Madras.

Table 1. Characteristics of WTR.

Parameter	Value
Acetone extract (%)	13
Carbon content (%)	39

Table 2. Formulation of the mixes.

	Mix No.				
Ingredient	A	B	C	D	E
NBR	100	90	80	70	60
Reclaim	–	20	40	60	80

NBR - Acrylonitrile butadiene rubber, (Zinc oxide – 4 phr, Stearic acid – 2 phr, HS (1,2-dihydro 2,2,4-trimethylquinoline) – 1 phr, MBTS (Dibenzothiazyl disulfide) – 0.5 phr, TMTD (Tetramethylthiuram disulfide) – 1.8 phr & Sulfur – 0.3 phr are common to all mixes).

Processing

Table 2 shows the formulation of the mixes. The mixes were prepared as per ASTM D 3182(1989) on a two roll laboratory size mixing mill. Cure characteristics of these mixes were found out using a Goettfert Elastograph Model 67.85 at 150°C. Vulcanization was carried out at 150°C under a pressure of 180 kg/cm^2 in an electrically heated hydraulic press. Vulcanizates were tested for different mechanical properties according to ASTM standards. Abrasion resistance was measured using DIN abrader as per DIN 53516. For ageing resistance, samples were aged in an air oven for 48 h and at 70°C.

RESULTS AND DISCUSSION

Cure Characteristics

MINIMUM TORQUE

The minimum torque values (Figure 1) show an increase at 20 parts of reclaim loading, beyond which it shows a decrease. The initial increase can be attributed to the filler content of the reclaim rubber. The reclaim contains about 39% carbon in addition to the plasticising oil. At higher reclaim loading the effect of plasticiser present in the reclaim become more predominant and the minimum torque values decrease.

(MAXIMUM–MINIMUM) TORQUE

The (maximum–minimum) torque values show a linear decrease with increase in reclaim content which can be attributed to the excess oil present in the reclaim. There is about 13% oil in the reclaim, as indicated by the acetone extract (Table 1). The lower molecular weight

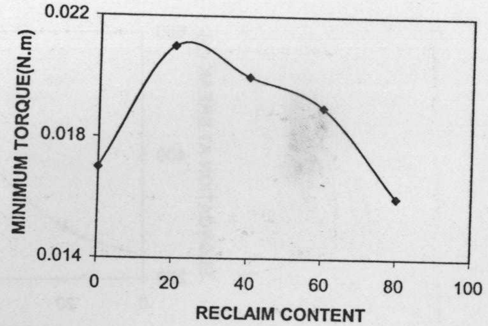

FIGURE 1. Variation of minimum torque with reclaim loading.

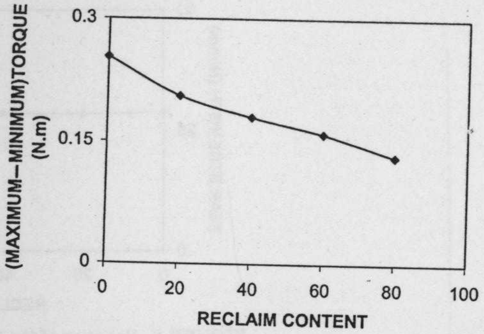

FIGURE 2. Variation of (maximum–minimum) torque with reclaim loading.

of the reclaimed rubber also contributes to the lower maximum torque values.

SCORCH TIME AND CURE TIME

Variation of scorch time with reclaim content is shown in Figure 3. The scorch time is more or less constant with only a marginal reduction at very high reclaim content. However, the cure time is drastically reduced even at 20 phr of reclaim loading (Figure 4). For mixes C–E, the cure time values are almost constant. The consistently lower cure times of the blends, compared to the gum compound can be attributed to the presence of unreacted curatives present in the reclaim. However, there is no corresponding increase in the cure rate (Figure 5). This suggests that as reclaim content increases the amount of reactive sites for cross linking decreases due to the partially cross-linked nature of reclaimed rubber.

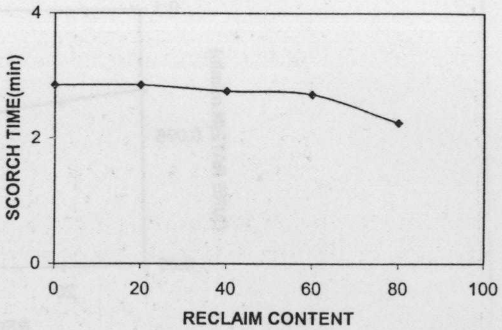

FIGURE 3. Variation of the scorch time with reclaim loading.

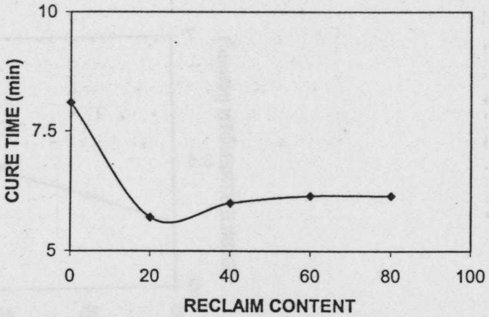

FIGURE 4. Variation of the cure time with reclaim loading.

MECHANICAL PROPERTIES

The variation of tensile strength with the addition of reclaimed rubber is shown in Figure 6. The tensile strength shows an almost linear increase with increasing reclaim content. This is in contrast to the results reported in the case of NR – reclaimed rubber blends. The difference can be attributed to the non-crystallizing nature of the NBR, which gives it poor gum strength. The presence of reinforcing filler in

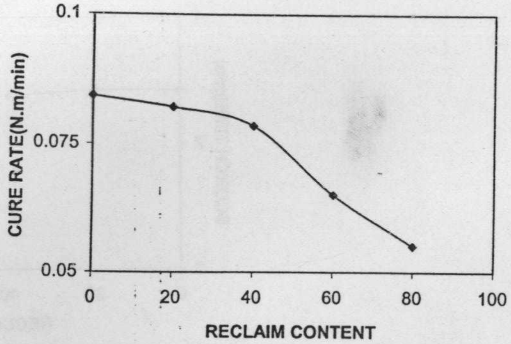

FIGURE 5. Variation of the cure rate with reclaim loading.

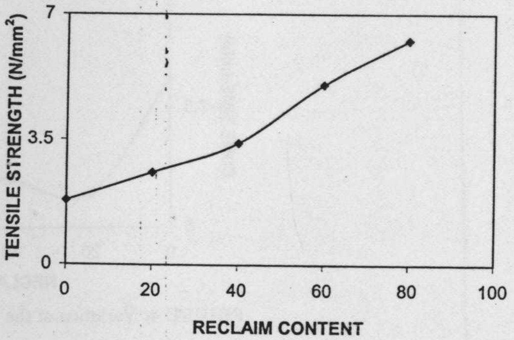

FIGURE 6. Variation of the tensile strength with reclaim loading.

the reclaim rubber can contribute to the tensile strength of NBR. In the case of NR – reclaim blend, the low gum strength reclaim cause more of dilution of the NR matrix than reinforcement. The elongation at break values (Figure 7) show an increase from 278% at 0 parts to 506% at 80 parts of reclaim content. The increase in elongation break can be attributed to the increasing amount of oil in the case of blends.

The tear strength values remain somewhat constant at all reclaim loading (Figure 8). The expected increase in tear strength values due to the presence of reinforcing black might have been offset by the lower molecular weight of reclaimed rubber.

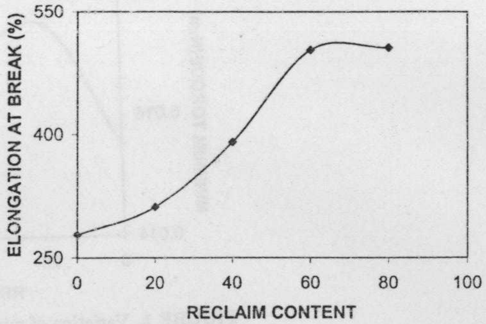

FIGURE 7. Variation of the elongation at break with reclaim loading.

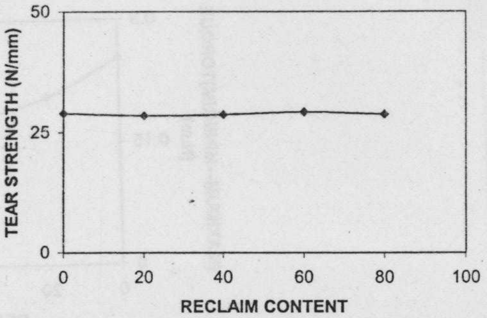

FIGURE 8. Variation of the tear strength with reclaim loading.

Figure 9 shows the heat generation values of the mixes. There is a gradual increase in heat build up values in the case of blends. Higher the concentration of filler higher is the chances of energy dissipation as heat. The energy dissipation can be through loss at filler – matrix interface, friction between the chains and breakdown of filler structure. This will be manifested as lower resilience values. As given in Figure 10, the resilience values show a linear decrease with increasing reclaim content.

Figure 11 shows variation of compression set at constant strain. The compression set increases with increase in reclaim loading. This is in agreement with the observed reduced resilience and increased hysteresis loss.

Figure 12 gives the abrasion loss of the blends containing different amounts of reclaimed rubber. The abrasion loss shows an increase with

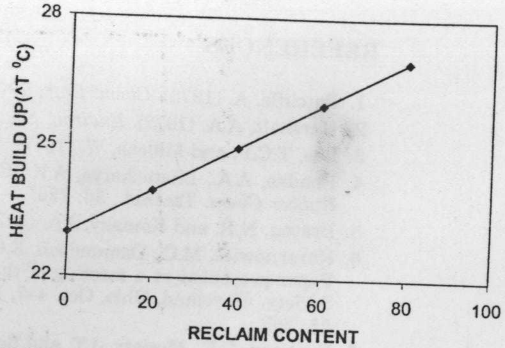

FIGURE 9. Variation of the heat build up with reclaim loading.

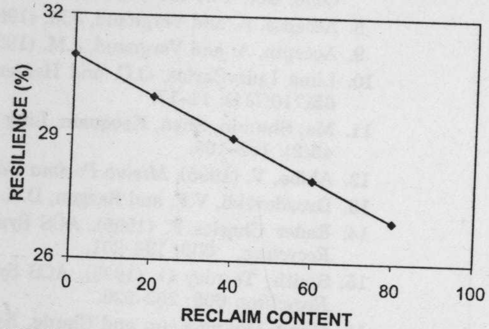

FIGURE 10. Variation of resilience with reclaim loading.

increase in reclaim content. The abrasion is a phenomenon involving tear hysteresis. Eventhough the tear resistance is almost constant, the hysteresis increases. This, combined with relatively lower molecular weight of the reclaimed rubber, gives rise to increased abrasion loss.

AGEING RESISTANCE

Table 3 shows the tensile properties of mixes before and after ageing. All mixes except the gum compound showed lower tensile strength values after ageing. The retention in the case of the gum compound (mix A) is 120%. This shows that the state of cure is improved while ageing. However, in the presence of reclaimed rubber in the blends there is some extent of degradation. This may be attributed to the fact that the reclaim mainly consists of natural rubber and it is more prone to degradation under elevated temperature.

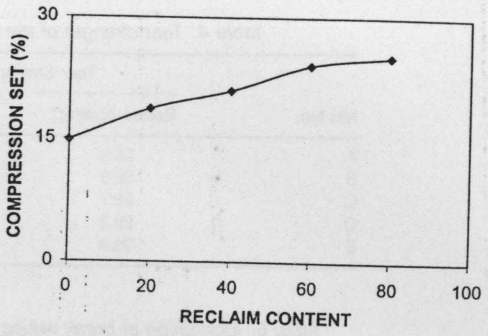

FIGURE 11. Variation of compression set with reclaim loading.

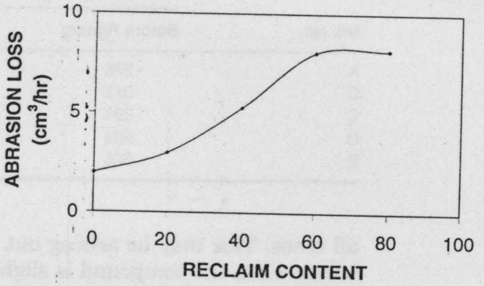

FIGURE 12. Variation of the abrasion loss with reclaim loading.

Table 3. Tensile strength of the mixes before and after ageing.

Mix No.	Tensile Strength (N/mm^2) Before Ageing	Tensile Strength (N/mm^2) After Ageing	Percentage Retention
A	1.8	2.2	120
B	2.6	2.3	89
C	2.6	2.5	92
D	5	4.7	94
E	6.3	5.7	91

Tear strength values before and after ageing are shown in Table. 4. The aged values are found to be lower than that of the unaged ones, in

Table 4. Tear strength of the mixes before and after ageing.

Mix No.	Tear Strength (N/mm)		Percentage Retention
	Before Ageing	After Ageing	
A	28.9	21.5	74
B	28.5	21	74
C	28.7	21.5	75
D	29.2	22.8	78
E	28.8	24.4	85

Table 5. Elongation at break values of the mixes before and after ageing.

Mix No.	Elongation at Break (%)		Percentage Retention
	Before Ageing	After Ageing	
A	278	292	105
B	312	285	91
C	391	324	83
D	504	451	90
E	506	490	97

all cases. This may be arising out of the fact that the tear strength is better when the compound is slightly under cured.

The elongation at break values of the blends after ageing is lower than that of the unaged samples (Table 5).

CONCLUSIONS

From the above study the following conclusions were drawn. Cure characteristics of NBR are affected by the incorporation of reclaimed rubber. Tensile strength of the NBR/reclaimed rubber blends increases with increase in reclaim content. Abrasion resistance, heat build up and resilience are adversely affected in the presence of reclaimed rubber. The elongation at break and compression set are increased. Ageing resistance of the blends are inferior to the gum NBR.

ACKNOWLEDGEMENTS

T. D. Sreeja is grateful to CSIR, Government of India for financial assistance.

REFERENCES

1. Ratcliffe, A. (1972). *Chem. Eng.*, **79**(7): 62.
2. Harshaft, A.A. (1972). *Environ. Sci. Technol.*, **6**(5): 412.
3. Lee, T.C.P. and Millens, W. (1977). *To Gould Inc.*, U.S. 4,046,834.
4. Phadke, A.A., Bhatacharya, A.K., Chakraborty, S.K. and De, S.K. (1983). *Rubber Chem. Technol.*, **56**: 726.
5. Braton, N.R. and Koutsky, J.A. (1974). *Chem. Eng. News*, **52**(6): 21.
6. Kazarnowicz, M.C., Osmundson, E.C., Boyle, J.F. and Savage, R.W. (1978). Paper presented at a meeting of the Rubber Division, American Chemical Society, Cleveland, Ohio, Oct. 4–7, 1977, abstract. *Rubber Chem. Technol.*, **51**: 386.
7. Peterson, L.E., Moriaty, J.T. and Bryant, W.C. (1978). Paper presented at a meeting of the Rubber Division, American Chemical Society, Cleveland, Ohio, Oct. 4–7, 1977, abstract. *Rubber Chem. Technol.*, **51**: 386.
8. Accepta, A. and Vergnaud, J.M. (1981). *Rubber Chem. Technol.*, **54**: 302.
9. Accepta, A. and Vergnaud, J.M. (1982). *Rubber Chem. Technol.*, **55**: 961.
10. Lima Luiz Carlos, O.C. and Hemans Carlos, A. (1997). *Rev. Quim. Ind.*, **65**(710/711): 11–17.
11. Ma, Shumin, Shen, Kaoquain, Ling and Guohua (1998). *Xiangjiao Gongye*, **45**(2): 102–105.
12. Akiba, V. (1995). *Misluo Porima Dayesuto*, **47**(10): 59–72.
13. Drozdovskii, V.F. and Razgon, D.R. (1995). *Kauch Rezina*, **2**: 2–8.
14. Rader Charles P. (1995). ACS Symp. Ser . *Plastics, Rubber and Paper Recycling*, **609**: 196–201.
15. Smith, Ternley G. (1995). ACS Symp. Ser. *Plastics, Rubber and Paper Recycling*, **609**: 202–220.
16. Hong, Houng-Keun and Chung, Kyung-Ho (1995). *Kongop Hwahak*, **6**(1): 1–7.
17. Magryta, Jack (1993). *Polymery.*, **38**(3): 132–135.
18. Gibala, D. and Hamed, G.R. (1999). *Rubber Chem. Tech.*, **72**(2): 357–360.
19. Seo, K.H. and Lim, H.S. (1998). *Polymer*, **22**(5): 833–838.
20. Theodore, Ares N., Pelt, Robert A. and Jackson, Danielle (1998). *Rubber World* **218**(2): 23–25.
21. Do, Quang Khang, Luum Due Hung and Nguyen (1997). *Van kWh Tap Chi Oh Hoc*, **35**(3): 33–36.
22. Phadke, A.A., Chakraborty, S.K. and De, S.K. (1984). *Rubber Chem. Technol.*, **57**: 19.
23. Chopey, N.P. (1973). *Chem. Eng.*, **80**(20): 54.
24. Burgogne, M.D., Leaker, G.R. and Kretic, Z. (1976). *Rubber Chem. Technol.*, **49**: 375.